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Section A.—Mathematical and Physical Sciences.

Spontaneous Incandescence of Substances in Atomic Hydrogen Gas.

By R. W. Wood, For. Mem. R.S.

(Received June 26, 1922.)

In a previous communication* it has been shown that if a very long vacuum tube of moderate bore, filled with hydrogen at a pressure of $\frac{1}{2}$ mm., is operated by a direct or alternating high potential current, the secondary spectrum appears only at the ends of the tube in the vicinity of the electrode bulbs, the central portion showing the lines of the Balmer series, with a faint trace only of the secondary spectrum. By this method photographs of the series down to the twentieth member were obtained. In more recent work the series has been photographed to the eighteenth line in the third order spectrum of a 7-inch plane grating with a lens of 20-feet focus, and the wave-lengths determined to within a few thousandths of an Ångström. This work will be described elsewhere. Practically all of the very peculiar effects described in the paper referred to above have been explained, and in the pursuit of some of the more elusive phenomena, some extremely interesting properties of atomic hydrogen gas have come to light which will be described briefly in the present paper.

The work developed out of a study of what I referred to in the earlier paper as "Infected Spots." It was frequently observed that white spots sometimes appeared along the central portion of the tube, which normally is fiery-purple in colour, and almost invisible through a green colour filter. These spots showed the secondary spectrum of hydrogen, with the full intensity exhibited at the ends of the tube, some fifty times as intense as in adjacent portions of the tube which gave the nearly pure Balmer spectrum.

* 'Roy. Soc. Proc.,' A, vol. 97 (1920).

Though I suspected that these infected spots, which often appeared quite suddenly and were difficult to get rid of, were in some way due to a contamination of the wall of the tube, I was quite unable to understand how they were produced, or why they caused the appearance of the secondary spectrum.

The accidental entrance into the tube of a minute speck of sealing-wax from the joint leading to the pump started the correct line of attack. Under the action of the powerful discharge the fragment was almost immediately reduced to a white spot of stannous oxide, and the hydrogen secondary spectrum at once appeared in its vicinity. After operating the tube for a few minutes, examination of the spot of oxide with a lens showed that it was covered with minute silvery globules of reduced tin.

I next tried fusing a fine wire of tungsten into the wall of the tube (which was of pyrex glass), fig. 1. The wire was raised to incandescence as soon as the discharge was started, and the secondary spectrum came out strong in its vicinity. This surprised me very much, as it seemed incredible that the wire could be brought to a white heat by any electrical action, and it appeared unlikely that the mere high temperature of the hydrogen was responsible. A thread of soft glass introduced into the tube was not melted, though completely immersed in the discharge. This showed that it was not high temperature of the gas that caused the incandescence of the wire. To test whether or not the secondary spectrum was in any way due to the emission of electrons by the wire and oxide speck, I arranged a small tungsten spiral in a side tube, out of the line of the discharge, and connected it to a well insulated storage battery. The spiral came to a red heat, however, *even when disconnected from the battery.* This indicated clearly that the heating of the wire was, in all probability, due to the action of the surface of the metal in causing re-combination of dissociation products of the discharge.

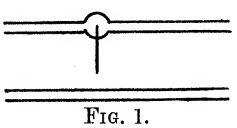

Fig. 1.

A platinum wire was next introduced into the discharge, but it remained non-luminous even with the heaviest current which could be brought to bear. With air at 0·5 mm. in the tube the platinum wire immediately came to a red heat, doubtless by causing the re-combination of nitrogen atoms.

During all of these experiments, pure electrolytic hydrogen entered one end of the tube through a very fine long capillary. No drying agent was employed, as the presence of the water vapour, which comes over with the hydrogen, is necessary for the production of the pure Balmer spectrum. The probable reason of this much discussed circumstance will appear presently.

As to the nature of the surface reaction which caused the heating of the

wire, it seemed probable that it was the re-combination of hydrogen atoms to form molecules, as the very small amount of oxygen present could hardly account for the phenomenon.

As was shown in the earlier paper, the secondary spectrum flashes out for a small fraction of a second when the current is first turned on; the duration of this flash was subsequently found* to be from 0·01 second (with 20 ampères in the primary of the transformer) to 0·04 second (with 2 ampères). If the switch is opened and kept open for a time in excess of about 0·2 second, the secondary flash can be obtained again on closing the switch; but if the time of the interruption of the current is much less than this, only the Balmer lines appear when the current is turned on again. The interruptions which occur during the normal operation of the tube, due to the passage of the potential of the transformer through the zero point, are too brief to allow the restoration of the condition necessary for the development of the secondary spectrum flash; in other words, the hydrogen remains in the atomic state. The simplest explanation of this is to consider that under the action of a heavy current practically all of the hydrogen in the central portion of the tube is kept permanently in the atomic condition, and hence only the Balmer lines appear.

Since the secondary spectrum flash does not appear when the current is broken, but only at the make, it seems safe to assume that the secondary spectrum is produced either by the continuous excitation of hydrogen molecules or by the explosion of the molecule into atoms, but not by the recombination of the atoms to form molecules. The great mystery was why the presence of water vapour or oxygen was necessary to suppress the secondary, and bring out the atomic, spectrum (Balmer series). I tried adding increasing amounts of oxygen to the hydrogen stream, by heating a small bulb containing crystals of permanganate of potash, joined to the tube by a short capillary. The tube contained a tungsten and a platinum wire; the former glowed at full incandescence while the latter remained dark. On gradually increasing the amount of oxygen, the tungsten wire cooled off and became black while the platinum wire grew first red then white hot.

The experiment was repeated with hydrogen dried by passage over P_2O_5. Neither wire heated until the oxygen stream was started, when the tungsten came to a white heat, and as more oxygen was added, cooled off again, the platinum heating in its turn as before. On cutting down the supply of oxygen the phenomena occurred in reverse order.

I discussed these results with Dr. Irving Langmuir, who has made an extended study of the atomic hydrogen produced by passing the gas over an

* 'Phil. Mag.,' vol. 43, pp. 9, 736 (1921).

incandescent surface of tungsten. He at once pointed out the property which oxygen has of "poisoning" a catalytic body. This explained why the addition of more oxygen stopped the heating of the tungsten, if we assume that the heating of the wire is caused by the catalytic action of its surface in bringing about the re-combination of the hydrogen atoms.

At an earlier period in the course of the experiments, when I first speculated on the possible formation of molecular hydrogen by the tungsten wire, I tried introducing the hydrogen through a capillary which opened directly into the discharge at a point near the middle of the tube, where only the Balmer lines appeared, fully expecting the secondary spectrum to appear in tht vicinity of the mouth of the capillary. To my great surprise, the discharge at the point remained fiery purple, with no increase in the intensity of the faint secondary spectrum.

As the hydrogen was flowing in at the rate of about 1 c.c. per minute, it seemed strange that it could be exploded into the atomic condition without giving any visible increase in the amount of secondary spectrum. Dr. Langmuir, however, made a calculation which shows that the wire may generate molecular hydrogen out of atomic at a much greater rate than the rate of inflow.

Assuming that the wire was 1 cm. long and 0·2 mm. in diameter, he found that it would take 4 watts to maintain it at 2,400° K. To supply this energy 0·25 c.c. of hydrogen (at atmospheric pressure) must be produced every second. This corresponds to 15 c.c. in 1 minute, or fifteen times as great as the rate of inflow. He further found that "when 1 grm. of hydrogen atoms combine to form molecular hydrogen, 45,000 small calories of heat are produced. In atomic hydrogen at 1 mm. pressure and 500° C. [my estimate of temperature of the gas in the tube, R.W.W.] the amount of hydrogen that strikes each square centimetre of surface per second is 0·0026 grm. This would produce a heating effect of 490 watts per square centimetre, which would be sufficient to heat a tungsten surface to 4100° absolute. Assuming the wire to be at 2400°, I calculated that this temperature could be maintained by a pressure of 0·16 mm. of atomic hydrogen in the tube, which seems a reasonable value."

It thus appears that the heating of the wire can be fully accounted for, and that the amount of molecular hydrogen generated from atomic is so much greater than the inflow from the capillary, that we need no longer be surprised at the failure of the secondary spectrum to appear at the point where the gas entered the discharge tube.

Langmuir's observation that the presence of minute traces of oxygen in the hydrogen prevents the formation of atomic hydrogen by a tungsten wire raised to incandescence in the gas by an electric current, and his suggestion that the oxygen must act in the same manner when a comparatively cool tungsten

wire is causing the recombination of the atoms, and absorbing the liberated heat, is of immense value in clearing up many of the mysteries of the hydrogen tube.

Previous to the experiments with the metallic wires I had found that if the inner surface of tube was fine ground with carborundum at a point near the centre, this portion of the tube remained always in the "white stage," *i.e.*, the secondary spectrum was strong and the Balmer series weak.

The ground surface evidently caused the recombination of the atomic hydrogen as fast as it was formed by the discharge, and the concentration never became great. Just why this was so was not at first apparent. Experiments with a thermocouple in the earlier work had shown that the temperature of the outer wall of the tube was always higher at the "infected spots" than on portions of the tube showing the Balmer lines only. The same was true of the ground-glass tube, the temperature rising to such a point that the D lines of sodium came out so strong that the discharge appeared yellow in spots.

The increase in the amount of glass surface exposed to the gas by the grinding could hardly account for the increased catalytic action, and it occurred to me that a fractured surface might be more active in bringing about the combination of the atoms. I accordingly made a pear-shaped bead of pyrex glass, scratched it across with a glass cutter and cracked it in two. This bead was suspended in the discharge by a glass fibre as shown in fig. 2.

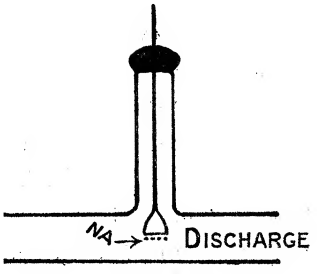

FIG. 2.

The cracked bead caused the discharge to become white in its vicinity while a whole bead could be immersed in the purple discharge without affecting it in the least. Moreover, the flat under-surface of the bead (the clean fracture) was seen to be covered with glowing sodium vapour, when the bead was viewed through a direct vision prism (to "spectroheliograph" it). This showed that the fractured surface had been raised to a very high temperature by the atomic hydrogen, while the fire-polished surface remained comparatively cool.

The action of other metals and oxides was next examined. A strip of very clean thin aluminium foil immersed in the purple discharge caused the appearance of the secondary spectrum in its vicinity, but after a few minutes' operation the white discharge in the vicinity of the narrow strip of foil disappeared, and the aluminium was as neutral to the atomic hydrogen as the fire-polished bead. Operating the tube with air in it restored the

aluminium to its original condition, and the white hydrogen discharge was again obtained.

It had frequently been observed, in working with long hydrogen tubes, that sometimes the white secondary spectrum discharge reached to a distance of 30 or 40 cm. from the electrode bulbs, while at other times, with pyrex tubes, carefully cleaned with hot chromic acid, and clean new aluminium electrodes, the purple discharge came up to within 2 or 3 cm. of the bulbs. It now seems probable that the secondary spectrum at the ends of the tube is due to the re-formation of molecular hydrogen by the more or less oxidised electrodes, in other words, the secret of obtaining the extended Balmer series by the use of a long tube lay in the utilisation of a portion of the tube far removed from the catalysing action of the electrodes.

A sufficiently powerful discharge is able to hold practically all of the hydrogen in the atomic condition. The secret of obtaining the complete Balmer series probably lies in obtaining a tube wall of zero catalysing power; I have tried fused quartz, but it appears to be no better than pyrex glass. Next autumn I plan to make a jointed tube of as many different types of glass as possible. It must be remembered, however, that it is the oxygen which brings the glass into the required condition.

A copper wire, strongly oxidised by a flame when introduced into the hydrogen tube, gave a strong secondary spectrum, and the surface immediately became of a bright metallic copper colour. Zinc oxide gave a black deposit on the glass wall in its vicinity. In these last two experiments the substances were in lateral tubes just outside of the discharge.

The most interesting material, however, was thorium oxide, with a trace of cerium (fragments of a Welsbach mantle). Small specks of this substance, visible only with a lens introduced into the tube, were scattered about by the discharge, and, adhering to the walls, glowed like first magnitude stars with a colour which appeared distinctly greenish, in contrast to the deep purple of the hydrogen discharge in which they were immersed. They produced no appreciable amount of secondary spectrum on account of their small size. Larger fragments produced strong secondary spectrum without coming to incandescence. This is to be expected, for if the atomic hydrogen acts upon too large a mass its energy of combination is distributed over too much material to bring it to incandescence. If, for example, we have a tungsten wire in a tube containing specks of thoria, the specks all glow brilliantly when the current is turned on. Presently the wire begins to act on the hydrogen, the secondary spectrum appears, and the incandescent thoria specks in the vicinity of the wire are immediately extinguished.

The ability of the tungsten wire to cause the re-combination of the atomic

hydrogen appears to depend to a certain extent on the condition of the surface. It was frequently observed that the wire did not heat until it had been immersed in the discharge for a minute or two, when it suddenly rose to incandescence; not until this change took place did the purple colour of the discharge change to white. After continued operation the wire often cooled down to a dull red heat. If the current was then shut off, and the wire allowed to rest for 5 or 10 minutes in the gas stream, it usually became white hot the moment the discharge was started again.

To investigate the flow of the atomic hydrogen out of the discharge tube the arrangement shown in fig. 3 was used.

Metallic wires, mounted on slender rods of glass, could be introduced through

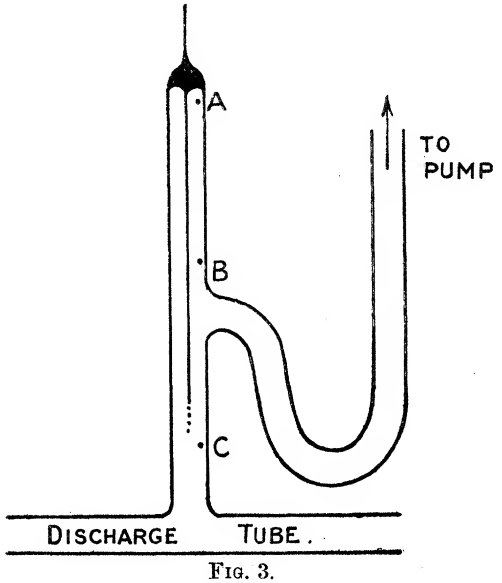

FIG. 3.

the tube A and placed at varying distances from the discharge, and the flow of the gas to greater distances could be followed by specks of thoria beyond the U-bend in the tube leading to the pump.

It was found that a tungsten wire could be maintained at a red heat at a distance of 4 cm. from the discharge tube (the tube was 5 mm. in diameter), while thoria particles were highly luminous at distances of 20 cm. or more. The increase in the free path of the atoms as the pressure was lowered was beautifully shown in one experiment, in which three thoria particles were attached to the wall at A, B, and C. In this case the current of hydrogen from the generator had been stopped and the pressure brought to 0·5 mm. On starting the discharge only the speck at *c* became incandescent. The

pump was then started, and, after a few revolutions, the particle at B lit up, and a few moments later the particle at A. The pump was then stopped and the pressure again measured. It had fallen to 0·15 mm. Cooling a portion of the tube at *c* with a cotton pad wet with liquid air, immediately extinguished all of the glowing thoria particles in the tube above *c*, which is in perfect agreement with an observation by Langmuir, that atomic hydrogen from a glowing tungsten wire will pass for a considerable distance along a glass tube, but will not pass a point cooled with liquid air.

The distance which the atomic hydrogen travelled along the tube to the pump, as shown by the glowing thoria, is in good agreement with the earlier observation that re-combination takes place in about one-fifth of a second, for the velocity of the gas down the tube is of the order of a metre per second.

It would be interesting to determine the life of atomic hydrogen in the absence of any catalysing surface, for the wall of the tube, even under the best conditions, appears to have some action (as shown by our inability to get rid of a faint trace of secondary spectrum).

I intend to try the conditions in a large glass bulb placed in the pump circuit as close to the discharge tube as possible. If the life of the atomic hydrogen is longer under these conditions, a speck of thoria at the centre of the bulb should continue to glow for a measurable time after the discharge is stopped.

There appears to be strong evidence that the discharge tube is filled with practically pure atomic hydrogen, not only during the flow of the current, but also during the brief intervals of low potential between the half-cycles of the alternating current, when no current is flowing in the tube. This suggests the possibility of determining the optical properties (refraction, dispersion, etc.) of atomic hydrogen, by including the discharge tube in one path of an interference apparatus, illuminated by light which is passed through two apertures in a disc mounted on the shaft of a synchronous motor. The illumination of the fringe system will then occur only when the gas in the tube is non-luminous.

Summary.

It is shown that some metals, oxides and other substances are raised to incandescence when introduced into a stream of atomic hydrogen, the surface of the substance acting as a catalyser in bringing about the recombination of the atoms.

Atomic hydrogen, practically free from molecular hydrogen, can be drawn by a pump from the central portion of a long vacuum tube, excited by a high potential current. Fire-polished glass surfaces, such as the wall of a

glass tube, have a comparatively feeble catalysing power; fractured surfaces, however, cause the recombination of the atoms, and are strongly heated.

The action of water-vapour or oxygen in enhancing the Balmer spectrum, and suppressing the secondary spectrum of hydrogen, is probably due to its action on the wall of the tube, which, when dry, catalyses the atomic hydrogen as fast as it is formed by the current.

The peculiar spectroscopic phenomena observed with long hydrogen tubes, and described in an earlier paper, are explained.

Methods are suggested for determining the physical and optical properties of atomic hydrogen gas.

On the Scattering of β-Rays.

By H. A. Wilson, F.R.S., Rice Institute, Houston, Texas, U.S.A.

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The scattering of β-rays by thin sheets of matter has been the subject of a number of experimental and theoretical investigations in recent years. J. A. Crowther and B. F. Schonland* give a good summary of the principal results so far obtained, together with an account of a new series of measurements.

Crowther and Schonland regard their experiments as decisively in favour of the theory of "single scattering," which was shown by Rutherford to account for the scattering of α-rays by thin plates in a thoroughly satisfactory way. In the case of α-rays the fraction of the rays scattered through considerable angles is very small, and it is on this that the success of the theory depends. In the case of β-rays the fraction scattered is very much larger, and it is difficult to believe that "multiple scattering" can be neglected.

On Rutherford's theory of single scattering each ray is supposed to be deflected by a single collision with an atom. The number of collisions is clearly proportional to the thickness (t) of the sheet, so that the fraction scattered through more than a given angle is also proportional to the thickness and

$$I/I_0 = 1 - kt, \qquad (1)$$

where I denotes the number of rays deflected through less than a given angle, I_0 the number of rays incident on the plate, and k is a constant.

* 'Roy. Soc. Proc.,' A, vol. 100, p. 526 (February, 1922).